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NATIONAL AMBIENT AIR QUALITY OBJECTIVES FOR GROUND-LEVEL OZONE

SCIENCE ASSESSMENT DOCUMENT

A report by the
Federal - Provincial Working Group
on Air Quality Objectives
and Guidelines

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Canada

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PREFACE

The Canadian Environmental Protection Act (*CEPA*), passed into law in 1988, replaces and builds upon the Clean Air Act and the Environmental Contaminants Act. The opening statement of the Act declares that "the protection of the environment is essential to the well-being of Canada". *CEPA* allows the Federal Government to assess substances and control their impact through national environmental quality objectives, guidelines, codes of practice, and/or regulations.

Provincial Governments have the primary responsibility in many areas of air pollution control, with federal actions integrated with those of the provinces. The *CEPA* Federal/Provincial Working Group on Air Quality Objectives and Guidelines (WGAQOG), consisting of representatives of federal, provincial and territorial departments of environment and health, reviews and recommends national ambient air quality objectives.

Canada's *National Ambient Air Quality Objectives(s) (NAAQOs)* prescribe targets for air quality, measured at the relevant receptor (persons, plants, animals, materials*). National Ambient Air Quality Objectives are national goals*[1] *for outdoor air quality that protect public health, the environment, or aesthetic properties of the environment*. The development of NAAQOs involves first, a scientific review of the physical and chemical properties of a substance, its sources, environmental, animal and human health effects, and an assessment of environmental and human exposure to the substance. Secondly, this information is integrated within a framework of risk assessment. The Science Assessment Document contains this critical scientific evaluation, and lays the scientific groundwork for establishing the air quality objectives. Reference Levels, levels above which there are demonstrated effects on human health and/or the environment, are identified. A document outlining the process followed in reviewing and interpreting the scientific information is published separately.[2] This document contains the scientific evaluation of Ground Level Ozone.

National Ambient Air Quality Objectives are targets for focussing air quality management strategies and plans. The derivation of these targets may consider some elements of benefit/risk analysis, reflecting a philosophy of environmental health protection and long term risk reduction while recognizing technological and economic limits. The broad range of potential responses by ecosystems, populations, and organisms in the environment are considered. Given the range of sensitivities within and among these environmental components, the resulting objectives may not protect all.

The process of establishing National Ambient Air Quality Objectives is a dynamic and

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[1] The Working Group develops NAAQOs for Federal/Provincial/Territorial and Municipal Governments to use as they deem appropriate. Implementation of air quality management strategies and standards is left to those agencies or to other national processes.
The definition in the text above, along with the descriptor provided above in this footnote, together comprise the new definition for NAAQOs.

[2] A Protocol for the Development of National Ambient Air Quality Objectives Part 1: Science Assessment Document and Derivation of the Reference Levels. WGAQOG, 1996.

continuous one. Air quality objectives are established to reflect the current state of knowledge about an air pollutant, to provide a national indicator for assessing the quality of air in all parts of Canada, and to provide guidance to governments for making risk management decisions such as planning control strategies and setting local standards.

It is recognized that not all locations in Canada will meet these air quality objectives immediately, or at all times, and that priority given to meeting these values may be based on factors such as available control technology, costs, benefits, and the degree to which the recommended objectives are exceeded. The expectation is that strategies will be implemented to facilitate the reduction of ambient air concentrations to a level at or below the air quality objective(s) as soon as practicable. The principles of continuous improvement and nondegradation of environmental quality are advocated.

NOTE:

In January 1998, Canadian Environment Ministers (with the exception of Québec) signed the Canada-Wide Accord on Environmental Harmonization and its sub-agreement on Canada-Wide Standards (CWSs). The CWS process provides new tools for the management of environmental issues of national interest. Recognizing that both NAAQOs and CWSs have a role to play in the management of air quality, federal, provincial, and territorial health and environment departments have integrated the NAAQO and CWS processes. Air pollutants that have been identified by governments as needing to be managed will be targeted for either CWS or NAAQO development, not both.

In January 1998, Environment Ministers identified ozone as a priority for Canada-Wide Standards. As a result, federal, provincial, and territorial health and environment departments agreed that NAAQOs for ozone will no longer be developed. Rather, this Science Assessment Document will form the Risk Assessment report for the development of CWSs for ozone.

NOTE:

This Science Assessment Document is, in general, a federal-provincial consensus document. One member of the WGAQOG, Alberta, does not, however, support some of the recommendations, including the form of the LOAEL for vegetation and the recommended Reference Levels for Human Health. This position is based on issues regarding the science and its application with respect to ozone impacts on health and the environment. Alberta nevertheless supports the publication of this document and believes that this document will make a positive contribution to the efforts of reducing ambient ozone levels in Alberta. More information on Alberta's position can be obtained from Alberta Environment, Environmental Sciences Division at (780) 427-5883 or from www.gov.ab.ca/env/protenf.html .

ACKNOWLEDGMENTS

This document has been prepared primarily as a compilation of material from the NO_x/VOC Science Assessment reports by the Multistakeholder NO_x/VOC Science Program. The authors of these reports are acknowledged for their significant contributions to this report. The individual reports that have been drawn upon for this assessment are:

- Ground-level ozone and it precursors, 1980 - 1993: Report of the Ambient Data Analysis Working Group (1997)
- Ground-level ozone and precursor monitoring guidelines and implementation plan: Report of the Ambient Air Monitoring Working Group (1997)
- Report of the Health Objective Working Group (1997)
- Report of the Vegetation Objective Working Group (1997)

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1 INTRODUCTION

The material contained within this report presents the current scientific and technical information relevant to the review of the present Canadian National Ambient Air Quality Objectives (NAAQOs) for ground-level ozone in air. This document has been prepared primarily as a compilation of the 1996 NO_x/VOC Science Assessment reports prepared under the auspices of the Multistakeholder NO_x/VOC Science Program. This material was augmented by an assessment of more recent literature on the human health effects of ozone, and the addition of material on the effects of ozone on materials and on animals. Recent literature on ozone effects on vegetation was also reviewed, but in consideration of the finding that there was no cause to alter the conclusions of the NO_x/VOC report on vegetation effects, the material was not updated. The information in this Science Assessment Document is based upon peer reviewed and publicly available information. The updated effects information is current to mid 1997. The individual reports which have been drawn upon for this assignment include:

- Ground-level ozone and its precursors, 1980-1993 — Report of the Data analysis Working Group (Multistakeholder NO_x/VOC Science Program, 1997)
- Ground-level ozone and precursor monitoring guidelines and implementation report— Report of the Ambient Air Monitoring Working Group (Multistakeholder NO_x/VOC Science Program, 1997)
- Report of the Health Objective Working Group (Multistakeholder NO_x/VOC Science Program, 1997)
- Report of the Vegetation Objective Working Group (Multistakeholder NO_x/VOC Science Program, 1997)
- National Air Pollution Surveillance Network Quality Assurance and Quality Control Guidelines (Mar, 1995)
- Canadian Emissions Inventory of Criteria Air Contaminants (1990) (Environment Canada, 1996)

The current Canadian Ozone Maximum Acceptable Air Quality Objective, developed in 1976 under the old three-tiered Framework for NAAQOs, is 82 ppb (parts per billion) with a one hour averaging time. This was reviewed in 1989 under the Canadian Environmental Protection Act (CEPA) and confirmed based upon the information available at that time.

This report constitutes the Science Assessment Document for ozone, which lays the foundation for the Risk Characterization and presents the rationale for the Reference Levels. Subsequent processes will develop the NAAQO(s) by considering technical, economic and social factors along with the scientific information as appropriate and feasible. The text is organized as follows:

- An introduction (1) provides contextual background information with following chapters on atmospheric chemistry (2), sampling and monitoring methods (3), and sources of ozone and its precursors to the environment (4).
- Chapter 5 summarizes the information on ambient environmental levels of ground-level ozone for remote, urban and rural monitoring stations, and discusses the factors contributing to ozone episodes.
- Chapters 6 through 11 present the scientific and health based information on exposure (6), the effects of ozone on materials (7), vegetation (8), birds and mammals (9), and on humans (10-12).
- The derivation of Reference Levels and the Risk Characterization are provided in Chapters 13 and 14.

The development of ambient air quality objectives for ground-level ozone is a difficult task due to the existence of identifiable and quantifiable impacts to more than one receptor: human health, vegetation and materials. The management of ground-level ozone is complicated by the fact that it is the product of complex secondary atmospheric chemical reactions.

Virtually none of the ground-level ozone measured in air is directly emitted from biogenic (natural) or anthropogenic (human) sources. Ozone is the product of a complex series of chemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOC). These primary pollutants, also known as precursor gases, are the products of combustion processes often associated with industry and the transportation sector. Some NO_x and VOC may be produced by biogenic sources, especially in summer when emissions from natural vegetation and agricultural crops, as well as associated management practices, are highest.

Local and regional meteorology are important factors in evaluating the severity and origin of ozone episodes, which tend to be associated with inversion conditions (which limit the dispersion of pollutants) and higher air temperatures and solar radiation from May through September.

Since high population density urban environments produce high levels of NO_x and VOC from transportation, ground-level ozone episodes are often most pronounced near these urban centres. In Canada, three areas have been identified as having excessively high numbers of days per year with ozone concentrations above the current NAAQO of 82 ppb. These are the Vancouver–Lower Fraser Valley area, where local physiography traps ozone during inversions; the Windsor-Québec City corridor (along the U.S. border and St. Lawrence River); and the southern Atlantic region. The latter two areas experience significant contributions due to long range transport of ozone and its precursors from the eastern and central or mid-west United States.

Since ground-level ozone co-exists in the atmosphere with other air pollutants prevalent in the urban environment, it is important to determine whether ozone acts alone or in combination with other common pollutants in affecting receptors. As this issue is not fully resolvable given current scientific understanding, this assessment will address only direct ground-level ozone receptor responses.

The effect of ozone on plants occurs when ozone enters the plant leaves disrupting oxidative photosynthesis processes and energy budgets of the plant, affecting leaves and roots. Damage to agriculture crops from ozone has been documented in Canada and the United States since the 1950s. Damage to forests near areas of high ozone concentration has also been reported. The effects of ozone on agricultural crops has been studied extensively, with highly variable sensitivities being reported due to differences in plant species, cultivars and growing conditions.

Effects of ground-level ozone on human health include reduced lung function, increased symptoms of respiratory discomfort and disease, and increased hospitalizations and emergency department visits, and death. There is evidence that ozone and particulate matter may act together in affecting human health when levels of both are elevated. Respiratory tract inflammation caused by ozone may predispose the tissue to the effect of particles. As with plants, there is wide variation in the response of the individual to ozone, with asthmatics being particularly sensitive.

A variety of materials have been shown to be susceptible to damage from exposure to ozone, including elastomers, textiles, painted surfaces, metals and masonry. Effects on metals and masonry are thought to be primarily the result of synergistic effects with sulphur dioxide. Cracking, fading, erosion and/or corrosion of materials are the principle effects observed.

There is relatively little information available on the effects of ozone on wildlife. The only significant exposure route is inhalation and therefore, the primary effects, as with humans, are respiratory. Indirect effects are also possible; for example ozone may affect the plants upon which wildlife feed.

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Multistakeholder NO_x/VOC Science Program, 1997. Report of the Health Objective Working Group. ISBN 1-896997-10-4

2 ATMOSPHERIC CHEMISTRY

The information in this chapter is based primarily on that presented in the Report of the Data Analysis Working Group (Multistakeholder NO$_x$/VOC Science Program, 1997).

2.1 CHEMICAL PROPERTIES

Ozone is a colourless gas at ambient air concentrations. In its pure, undiluted form the gas has a dark bluish colour. The three oxygen molecules are linked at an angle of 116°49'±30' with a distance between the atoms of 1.278±0.003Å. The basic physical properties of ozone are listed in Table 2.1 (Lide, 1996).

Table 2. 1 Physical and Chemical Properties of Ozone

Physical State	Gas
Physical Description	Coloured gas with pungent odour
Molecular Formula	O_3
Melting Point	-192.7±2°C
Boiling Point	-111.9°C
Density	
gas	2.144 gm/l @ 0°C
liquid	1.614 gm/l @ -194°C
Water Solubility	49cm^3 @ 0°C
Vapour Pressure	1mm Hg @ -180.4°C
CAS Number	10028-15-6
Henry's Law Constant	4.57x10^{-3} @ 20°C
Molecular Weight	47.9982
Common Valences	4 primary structures with strong delocalized B bonding
Rate Constants	
Photolysis	Complex, see Section 2.2
Oxidation/photo-oxidation	
Hydrolysis	

Ozone is a strong, gaseous oxidizing agent which reacts rapidly with other atmospheric constituents. Ozone is one of a number of photochemical oxidants in the lower atmosphere that are produced as a consequence of chemical reactions involving sunlight. The formation of ozone (and other atmospheric oxidants) is the result of complex non-linear physical and chemical processes in the atmosphere, including two classes of precursor pollutants: NO_x (nitrogen oxides) and VOC (volatile organic compounds). Thus, in the lower atmosphere, ozone is primarily a secondary pollutant formed from gaseous precursors. Both atmospheric chemistry and meteorological processes have significant roles to play in the formation and transport of ground-level ozone.

2.2 ATMOSPHERIC OXIDANT CHEMISTRY

2.2.1 Sources

The sources of tropospheric ozone are: 1) direct transport from the stratosphere (stratospheric ozone) and 2) photochemical formation from natural and anthropogenic precursors within the lower troposphere. Of these two sources, the latter, is thought to represent the largest source of ground-level ozone (Logan, 1985).

Stratospheric Ozone

In the stratosphere, ozone (O_3) and oxygen (O_2) are part of a natural cycle of formation and destruction that is driven by energy from the sun. Ozone is formed by the photodestruction of oxygen into separate atoms that react with other molecules of oxygen to yield ozone molecules. In turn, the breakdown of ozone and release of molecular oxygen are also triggered by the absorption of UV light. Ozone is distributed throughout the atmosphere, but its concentration varies greatly with altitude. Most of the ozone is concentrated in the middle stratosphere, in a band commonly referred to as “the ozone layer”. In the stratosphere, ozone is not a pollutant. Rather it serves a critical function in preventing the penetration of much of the UV light that would otherwise be damaging to life on earth.

There is evidence that some stratospheric ozone is transported down to the free troposphere (Altshuller, 1986; Mukammal et al., 1985; Wakamatsu et al., 1989) contributing to the total ozone observed close to the ground. Under normal conditions, there is little exchange between the lower stratosphere and upper troposphere in mid-latitude regions. However, this situation can dramatically change when deep troughs develop at the tropopause, producing large-scale eddies that carry ozone-rich air parcels downward to the free troposphere. In the northern hemisphere, spring weather conditions appear to favour stratospheric ozone intrusion into the troposphere, coinciding with the periods of highly mobile westerlies. It is estimated that this transport mechanism contributes less than 10 ppb to annual average ground-level ozone (Altshuller, 1986).

Photochemical Ozone Formation in the Troposphere

Tropospheric ozone is formed and destroyed in a series of reactions involving nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)). Nitric oxide, introduced into the troposphere from various natural and anthropogenic sources, reacts rapidly with ozone to form NO_2 (R1). Nitrogen dioxide absorbs sunlight in the ultraviolet and visible range (280 nm < λ < 430 nm) and photodissociates to yield oxygen atoms (O) and NO (R2). The oxygen atoms rapidly combine (time constant $\tau_o \sim 13 \mu s$ (Finlayson-Pitts and Pitts, 1986)) with molecular oxygen (O_2) to produce ozone (R3). The M in R3 represents a third molecule (N_2 or O_2) that absorbs the excess vibrational energy that is released by this reaction and thereby stabilizes the newly formed ozone molecule (Seinfeld, 1986). Reactions R2 and R3 are always the final steps in ozone formation in the troposphere (Warneck, 1988).

Formation and destruction of ozone

NO	+	O_3		$\rightarrow$	NO_2	+	O_2	R1
NO_2	+	$h\nu$		$\rightarrow$	NO	+	O	R2
O_2	+	O	+ M	$\rightarrow$	O_3	+	M	R3

In the absence of other chemical species, reactions R1 to R3 govern ozone formation, and a steady state is achieved in which ozone and O are continuously being formed and destroyed (Seinfeld, 1986). Thus, under steady-state conditions, the ozone concentration $[O_3]$ is given by

$$[O_3] = \frac{j_1}{k_1} \frac{[NO_2]}{[NO]} \qquad [1]$$

where k_1 and j_1 are the reaction ($k1$ = 26.59 ppm^{-1} min^{-1} at 25 °C) and photolysis ($j_1 \sim 0.533$ min^{-1} during midday in the summer) rate constants for reactions R1 and R2 (Seinfeld, 1986). Several workers have pointed out that measured ozone concentrations are significantly higher than those calculated from [1] in both urban and rural atmospheres (Kelly et al., 1984; Logan, 1985). This shows that the ratio of $[NO_2]/[NO]$ cannot be controlled only by reactions R1-R3; there must be other reactions that convert NO to NO_2 without consuming ozone in situations where ozone concentrations are abnormally high.

The Role of Hydrocarbon Oxidation in Ozone Formation

The atmosphere is never free of chemical species that interfere with the pathway outlined by reactions R1-R3, even in remote locations. In polluted urban atmospheres, elevated levels of hydrocarbons (denoted here as RHs) and NO_x play important roles in ozone formation. Under conditions where hydroxyl radicals can be formed photochemically, hydrocarbons are degraded to produce peroxy radicals ($RO_2^{\bullet}$), which react with NO to produce NO_2 (Atkinson, 1985; Singh, 1987; Warneck, 1988). Therefore, as noted above, these reactions convert NO to NO_2 without destroying ozone. This process can be visualized as follows (other pathways are possible but they are not described here):

Ozone formation (role of hydrocarbon oxidation)

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \qquad R4$$

$$R^{\bullet} + O_2 + M \rightarrow RO_2^{\bullet} + M \qquad R5$$

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \qquad R6$$

$$RO^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + (RCHO \text{ and/or } R_1R_2CO) \qquad R7$$

$$HO_2^{\bullet} + NO \rightarrow NO_2 + HO^{\bullet} \qquad R8$$

$$2\,(NO_2 + h\nu) \rightarrow 2(NO + O) \qquad R2$$

$$2(O + O_2 + M) \rightarrow 2(O_3 + M) \qquad R3$$

$$\text{Net:} \quad RH + 4O_2 + h\nu \rightarrow 2O_3 + H_2O + (RCHO \text{ and/or } R_1R_2CO)$$

A chain of reactions is initiated when RHs react with the hydroxyl radical ($HO^{\bullet}$) (R4) to form water vapour (H_2O) and alkyl radicals ($R^{\bullet}$), which subsequently react with O_2 (R5) to produce alkylperoxy radicals ($RO_2^{\bullet}$). $RO_2^{\bullet}$ in turn reacts with NO (R6) to yield NO_2 and alkoxy radicals ($RO^{\bullet}$), which rapidly combine with O_2 (R7) to produce hydroperoxy radicals ($HO_2^{\bullet}$), aldehydes (RCHO) and/or ketones (R_1R_2CO) (Singh, 1987). The sequence of reactions leading to ozone is completed with R8, R2 and R3, according to which two ozone molecules are formed for each RH molecule converted to RCHO or R_1R_2CO. The well-known observation that ozone concentrations tend to be higher in rural locations downwind of an urban pollution source is consistent with ozone being a secondary pollutant whose formation requires time for the oxidation of hydrocarbons.

In addition to anthropogenic sources, biogenic hydrocarbons emitted by deciduous (isoprene) and coniferous (monoterpenes) forests can act as significant precursors for ozone (Lloyd et al., 1983; Trainer et al., 1987). Biogenic hydrocarbons can significantly affect ozone levels even in urban atmospheres, downwind from emission sources (Chameides, 1988), and their presence can exert a profound influence on the effectiveness of ozone abatement strategies based on curtailed emissions of anthropogenic hydrocarbons and NO_x (U.S. N.R.C., 1991). Measurements and model results at a rural site in central Ontario (Lin et al., 1991) have also demonstrated that natural hydrocarbons, such as isoprene, can significantly contribute to local ozone formation.

The actual situation is more complicated than is implied by Reactions R2 - R8 for two reasons. First, RCHO and R_1R_2CO are themselves substrates for further oxidation, and additional ozone will be generated in each cycle of oxidation until the original hydrocarbons have been completely oxidized to carbon dioxide (CO_2). Considerable work has been done to estimate the overall yield of ozone per molecule of individual precursor hydrocarbons, both anthropogenic and biogenic (Chameides et al., 1992; Carter, 1994; de Leeuw, 1993). The yield of ozone per molecule of precursor is not a straightforward quantity to estimate because it depends on both the amount of the precursor available for oxidation and the rate at which it is attacked by $HO^\bullet$. Highly reactive precursors, particularly alkenes, have a strong impact on air quality because their rapid oxidation produces a "pulse" of ozone close to the site of emission.

The second factor is that not all $HO_2^\bullet$ radicals produce ozone through the sequence R8, R2, R3, because the ozone-consuming reaction R17 competes for $HO_2^\bullet$(see section 2.2.2). The net production of ozone is determined by the relative rates of reactions R8 and R17. In the polluted urban troposphere ("high NO_x" chemistry), the potential for ozone formation is much higher than in remote areas ("low NO_x" chemistry). The mechanism described here explains why both RHs and NO_x are necessary for the occurrence of ozone episodes.

The secondary oxidation of RCHO and R_1R_2CO with $HO^\bullet$ can lead both to generation of additional ozone and to other products (Atkinson, 1985), the most important of which (from the pollutant viewpoint) are the alkyl and acyl nitrates, such as peroxyacetyl nitrate (PAN: $CH_3C(O)$-O-O). PAN is a noxious compound that is formed by a sequence of reactions from the acetyl radical ($CH_3C(O)^\bullet + O_2 \rightarrow CH_3C(O){-}O{-}O^\bullet$, followed by reaction with $NO_2 \rightarrow CH_3C(O){-}O{-}O{-}NO_2$). The rate of breakdown of PAN back to $CH_3C(O){-}O{-}O^\bullet$ and NO_2 is strongly temperature-dependent; it decomposes thermally in the lower troposphere in warm weather with a half-life of a few hours, but is stable for long periods in the upper, colder troposphere (Finlayson-Pitts and Pitts, 1986), where it can be transported long distances.

Sources of Hydroxyl Radicals

The dominant sources of $HO^\bullet$ are photochemical; therefore, both its formation and the subsequent formation of ozone are mainly daytime events. The principal route for forming $HO^\bullet$ is through the photochemical dissociation of ozone (R9), which produces O_2 and excited oxygen atoms ($O^\bullet$); the latter subsequently react with H_2O to form $HO^\bullet$ (R10). Photolysis of nitrous acid (HNO_2) to yield NO and $HO^\bullet$ (R11) is normally a secondary source of $HO^\bullet$, but may sometimes be predominant during the early morning. Photochemical dissociation of RCHO and R_1R_2CO can also lead indirectly to $HO^\bullet$ formation. For instance, the photolysis of RCHO produces formyl ($HCO^\bullet$) and $R^\bullet$ radicals (R12). $R^\bullet$ will react with O_2 (R5) to yield $RO_2^\bullet$, which produces $HO^\bullet$ via reactions R6-R8; $HCO^\bullet$ will form carbon monoxide (CO) and $HO_2^\bullet$, which also leads to $HO^\bullet$ formation (R8). Note that while RCHO and R_1R_2O are emitted into the atmosphere as primary pollutants, they are also produced as secondary pollutants through hydrocarbon oxidation (R4-R8). Their subsequent photolysis causes further ozone production via the pathway R12-R13-R8-R2 and the production of more $HO^\bullet$ radicals, which speed up both the overall rate of hydrocarbon oxidation and the formation of ozone.

Hydroxyl radical formation

$O_3 + h\nu \rightarrow O^\bullet + O_2$ R9

$O^\bullet + H_2O \rightarrow 2HO^\bullet$ R10

$HNO_2 + h\nu \rightarrow NO + HO^\bullet$ R11

$RCHO + h\nu \rightarrow R^\bullet + HCO^\bullet$ R12

$R^\bullet + O_2 + M \rightarrow RO_2^\bullet + M$ R5

$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2$ R6

$RO^\bullet + O_2 \rightarrow HO_2^\bullet + (RCHO \text{ and/or } R_1R_2CO)$ R7

$HCO^\bullet + O_2 \rightarrow CO + HO_2^\bullet$ R13

$HO_2^\bullet + NO \rightarrow NO_2 + HO^\bullet$ R8

The major sink for $HO^\bullet$ is reaction with NO_2, which leads to the formation of HNO_3 (R14); reaction 15 can become important when NO_2 is low.

Hydroxyl radical sink

$HO^\bullet + NO_2 + M \rightarrow HNO_3 + M$ R14

$HO^\bullet + HO_2^\bullet \rightarrow H_2O$ + Hydroxyl Radical Sink R15

2.2.2 Sinks

Ozone is removed from the troposphere through several processes, including gaseous and aqueous chemical destruction, and deposition at the ground. Of these, it appears that the deposition at the ground dominates the ultimate depletion process (Galbally & Roy, 1980).

Gaseous Chemical Reactions

As a reactive trace component of the atmosphere, ozone can be scavenged by reaction with various free radical (odd electron) species. In polluted atmospheres, the most readily available atmospheric sink for ozone is reaction R1. Reaction R2 does not operate at night and R1 can lead to a complete removal of ozone when sufficient NO is present. In unpolluted atmospheres, NO concentrations are too low to scavenge ozone appreciably. Therefore, nighttime ozone concentrations in rural areas are normally higher than those in urban locales.

Ozone reacts with NO_2 to produce a nitrate radical ($NO_3^{\bullet\bullet}$) and O_2, or NO and O_2 (R18, R19; Singh, 1987). The newly formed $NO_3^{\bullet\bullet}$ can react with NO_2, producing nitrogen pentoxide (N_2O_5), which combines with water to form HNO_3 (R20 and R21). $NO_3^{\bullet\bullet}$ is very rapidly photolysed (to NO_2 and O) and therefore reactions involving $NO_3^{\bullet\bullet}$ are unimportant during daytime (Singh, 1987; Warneck, 1988). On the other hand, $NO_3^{\bullet\bullet}$ is quite reactive and can take over the role of $HO^\bullet$ in keeping radical chemistry active when $HO^\bullet$ cannot be formed photochemically. Ozone is also reactive with $HO_2^\bullet$ and $HO^\bullet$ (R16 and R17). These processes are especially important when the NO_x concentrations are low, as in unpolluted atmospheres.

Chemical reactions leading to ozone destruction

$$O_3 + HO^\bullet \rightarrow HO_2^\bullet + O_2 \qquad R16$$

$$O_3 + HO_2^\bullet \rightarrow HO^\bullet + 2O_2 \qquad R17$$

$$O_3 + NO_2 \rightarrow NO_3^{\bullet\bullet} + O_2 \qquad R18 \qquad \rightarrow \qquad NO + 2O_2 \qquad R19$$

$$NO_3^{\bullet\bullet} + NO_2 \rightarrow N_2O_5 \qquad R20$$

$$N_2O_5 + H_2O_{(1)} \rightarrow 2HNO_3 \qquad R21$$

$$O_3 + RH \rightarrow CO + HO_2^\bullet + HCHO + \text{other products} \qquad R22$$

In addition to acting as precursors for ozone, unsaturated hydrocarbons also act as sinks. The most important reactions of ozone with tropospheric alkenes are those with ethylene (C_2H_4), propylene (C_3H_6) and butene (C_4H_8) (Henderson et al., 1990; Seinfeld, 1986), as well as biogenic hydrocarbons such as isoprene and monoterpenes (Altshuller, 1983).

Aqueous Chemical Reactions

Ozone can act as an oxidizing agent for several chemical species in solutions (Lelieveld & Crutzen, 1990; Finlayson-Pitts & Pitts, 1986). The importance of these processes is, of course, dependent upon the extent to which the species dissolve in water. Ozone can act as an oxidizing agent for sulphur dioxide (SO_2) in aqueous droplets. In the aqueous phase, SO_2 is converted to bisulphite (HSO_3^-) (R23), which is oxidized by ozone to sulphate anion (SO_4^{2-}) (R24). Modelling indicates that reaction R24 can represent a significant sink for ozone in moist atmospheres rich in SO_2, especially during continuous precipitation. However, the pH of SO_2 solutions is usually less than 5 on account of reaction R23 and, under these conditions, oxidation of SO_2 with H_2O_2 is the predominant pathway for the production of SO_4^{2-} (Schwartz, 1984). Nitrite ion (NO_2^-), which is formed by the dissociation of dissolved HNO_2, can likewise be oxidized to nitrate ion (NO_3^-) by ozone (R28). The importance of reaction R28 as a sink for ozone is small due to low NO_2^- concentrations found in dew, cloud and rain-water (Lee and Schwartz, 1981). However, this mechanism of ozone scavenging could be more important in polluted atmospheres where concentrations of nitrogen compounds are relatively high.

Aqueous phase ozone destruction involving SO_2 or NO_x

$SO_{2(g)} + H_2O_{(l)} \rightarrow H^+ + HSO_3^-$ R23
$HSO_3^- + O_{3(aq)} + OH^- \rightarrow SO_4^{2-} + H_2O + O_{2(aq)}$ R24
$NO_{(g)} + NO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + 2NO_2^-$ R25
$2NO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + NO_3^- + NO_2^-$ R26

$HNO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + OH^- + NO_2^-$ R27

$NO_2^- + O_{3(aq)} \rightarrow NO_3^- + O_{2(aq)}$ R28

The study by Lelieveld and Crutzen (1990) suggests that aqueous phase reactions involving free radicals may destroy ozone directly, and also indirectly decrease the rate of ozone formation by scavenging $HO_2^\bullet$ radicals from the gas phase into water droplets. Some of the dissolved $HO_2^\bullet$ undergoes dissociation to form H^+ and superoxide ions (O_2^-), which rapidly react with ozone and in the process produce OH^- and $HO^\bullet$ (R29 and R30). Thus a cycle of reactions (R29 to R32) is established in which ozone and H_2O_2 are converted to molecular oxygen and water. The intervention of this mechanism (R29 to R32) in moist atmospheres will suppress reaction R8 by inhibiting $HO^\bullet$ formation, thus reducing the rate of ozone formation by reactions R2-R8. Model calculations (Lelieveld & Crutzen, 1990) suggest that in the presence of clouds, tropospheric ozone formation could be decreased by up to 30% through reactions R29 to R32, compared with cloudless conditions.

Aqueous phase ozone destruction involving free radicals

$HO_{2(aq)} \rightarrow H^+ + O_2^-$ R29

$O_2^- + O_{3(aq)} + H_2O_{(l)} \rightarrow OH^- + HO^\bullet + 2O_2$ R30
$OH^- + H^+ \rightarrow H_2O_{(l)}$ R31
$HO^\bullet + H_2O_{2(aq)} \rightarrow HO_{2(aq)} + H_2O_{(l)}$ R32

Net: $O_3 + H_2O_{2(aq)} \rightarrow 2O_{2(aq)} + H_2O_{(l)}$

Ozone Deposition to Vegetation and Other Terrestrial Surfaces

Ozone is readily deposited to vegetation and other terrestrial surfaces in a process known as dry deposition. This process is, to some extent, controlled by the turbulent exchange characteristics of the atmosphere and largely by the properties of the underlying surface (receptors). Taller plant canopies efficiently deplete ozone from the atmosphere (Fowler et al., 1989; Fuentes et al., 1993; Galbally & Roy, 1980; Hosker & Lindberg, 1982) due to the strong turbulent mixing in the overlying air. Turbulent diffusion transports ozone from the free atmosphere to the vicinity of the receptor surface, but surface processes determine the final step in the transfer and uptake mechanism. In the case of foliage, ozone molecules diffuse into the stomatal cavities of leaves, where they rapidly react with compounds present in the membranes of cells beneath these stomatal cavities (Chameides, 1989). There is evidence that the ozone concentration inside stomatal cavities is nearly zero (Amiro & Gillespie, 1985; Chameides, 1989), suggesting that ozone is consumed almost immediately after it arrives at the cell walls of stomatal cavities. Other terrestrial surfaces, such as soil, building structures and water, can also take up and contribute to the removal of O_3 from the lower troposphere (Galbally & Roy 1980; Wesely et al., 1981).

2.3 GROUND LEVEL OZONE PRECURSORS

A brief overview of the physical and chemical characteristics of the precursors NO_x and VOC is provided to give overall context to the formation of ground level ozone. Ambient levels, and the environmental and health effects of the precursors will not be addressed in this assessment.

2.3.1 Nitrogen Oxides

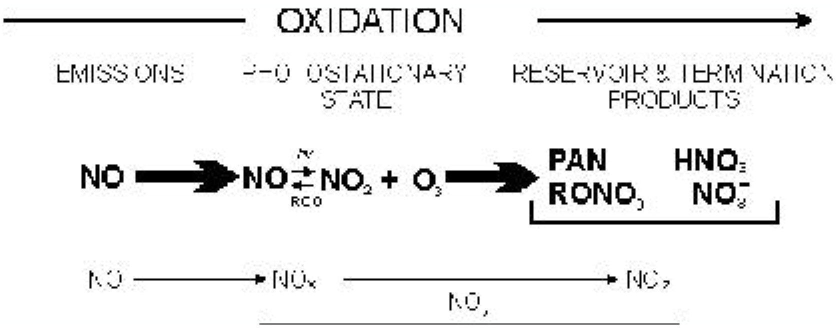
Several chemical symbols (NO_x, NO_y and NO_z) are used to represent the different groups of nitrogen oxide species that are important in the troposphere (Olszyna et al., 1994). These species are determined from measurements of related compounds, as shown in Table 2.2 and Figure 2.1. The family of tropospheric reactive oxidized nitrogen species, generically referred to here as NO_y, is composed of principally NO, NO_2, peroxyacetyl nitrate (PAN), HNO_3 and NO_3-aerosol. Other inorganic and organic species may make additional minor contributions to the total family concentration. These species play several significant roles in tropospheric photochemistry. The primary pollutant, NO, is ultimately oxidized to HNO_3(nitric acid). Removal of nitric acid from the atmosphere by wet and dry deposition constitutes the oxidized nitrogen contribution to acid deposition, which in eastern North America is significant; second to sulphate deposition. Organic peroxy and hydroperoxy radicals are responsible for much of the oxidation of NO to NO_2; hydroxyl radicals oxidize NO_2 to HNO_3 and peroxyacetyl radicals combine with NO_2 to form PAN (see chemistry discussion in Section 2.2). These reactions exert a controlling influence on the radical balance in the troposphere. To the extent that the products are removed from the atmosphere before dissociating, these reactions provide sinks for the radicals and thus also affect the total radical concentration in the troposphere. Since the radicals are responsible for forming the major oxidants of the troposphere (ozone, hydrogen peroxide and organic hydroperoxides), the levels of these oxidants are strongly coupled to the levels of the NO_y

family. The characterization of the levels of these species is therefore essential to the understanding of tropospheric photochemistry.

Table 2.2 Nitrogen Oxides -- Species and Terminology

Formula/Abbreviation	Compound/Definition
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	$= NO + NO_2$
PAN	Peroxy Acetyl Nitrate
HNO_3	Nitric Acid
NO_3^-	Particulate Nitrate
RNO_3	Organic Nitrate
HONO	Nitrous Acid
NO_z	$= PAN + HNO_3 + NO_3^- + HONO + RNO_3$
NO_y	$= NO_x + NO_z$

Figure 2. 1 Nitrogen Oxide Species that Participate in Atmospheric Photooxidation (after Olszyna et al. 1994)



2.3.2 *Volatile Organic Compounds (VOC)*

Volatile organic compounds, or VOC, are generally defined as compounds containing at least one carbon atom (excluding carbon dioxide and carbon monoxide) and with a vapour pressure of 0.01 kPa or greater at 25°C. Although there are many thousands of organic compounds in the natural and polluted troposphere that meet the definition of a VOC, most measurement programs have concentrated on the 50 to 150 most abundant C_2 to C_{12} hydrocarbons consisting of the general formula C_xH_y and on C_2 to C_6 carbonyls (compounds that, in addition, contain the structural element :C=O). The categories of VOC most relevant to ground-level ozone formation are summarized in Table 2.3. For this report, total non-methane hydrocarbons (total NMHC) are defined as the sum of all identified C_2 to C_{12} hydrocarbons of formula C_xH_y. Total VOC are defined as total NMHC plus carbonyls. Other categories of VOC, such as halogenated hydrocarbons and methane, are not included in this chapter. Initiated by the presence of sunlight and nitrogen oxides, ozone formation includes a complex array of reactions involving the atmospheric oxidation of VOC. In this process, individual VOC differ in their efficiency towards ozone formation. Therefore, a scale in which each compound is ranked according to its potential to form ozone has long been considered for selective regulation of emissions rather than an approach that treats all VOC equally. Depending on the ranking procedure, different terms have been used to denote the ability of an organic compound to contribute to the formation of ozone. Examples include photochemical ozone-forming potential, incremental reactivity or, simply, reactivity (Paraskevopoulos et al., 1995).

Table 2.3 Important Categories of Volatile Organic Compounds

Category	Example Compounds	Carbon Atoms	Molecular Weight (g/mole)	Propy-Equiv Factor $K_{OH}/K_{OH,Prop}$	MIR[3] (mole O_3/moleC)
Alcohol	Methanol	1	32	0.04	0.37
	Ethanol	2	46	0.12	0.65
Alkane	Ethane	2	30	0.01	0.08
	Propane	3	44	0.04	0.15
	n-Butane	4	58	0.10	0.31
	Hexane	6	86	0.21	0.29
Alkene	Ethylene	2	28	0.32	2.12
	Propylene	3	42	1	2.74
	1-Butene/Isobutene	4	56	1.20	2.10
	trans-2-Pentene	5	70	2.55	2.57
Alkene (Biogenic)	Isoprene	5	68	3.84	2.57
	a-Pinene	10	136	2.03	0.93
Alkyne	Acetylene	2	26	0.03	0.14
Aromatic	Benzene	6	78	0.05	0.11

---

[3] MIR Carter maximum Incremental Reactivity

	Toluene	7	92	0.22	0.74
	m and p-Xylene	8	106	0.77	2.07
Aldehydes	Formaldehyde	1	30	0.37	4.39
	Acetaldehyde	2	45	0.60	2.56
Ketones	Acetone	3	53	0.01	0.21
Ether	Methyl t-Butyl Ether	5	88	0.11	0.23

The species ethylene, m and p-xylene, toluene, propylene and 1,2,4-trimethylbenzene are the most important contributors to reactivity-weighted (using Carter maximum incremental reactivity method [MIR]) total hydrocarbon levels (Table 2.3).

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3 MONITORING TECHNOLOGIES

The information in this chapter is based primarily on that presented in the Report of the Data Analysis Working Group (Multistakeholder NO_x/VOC Science Program, 1997).

The pollutants of interest for assessing ozone pollution are ozone (O_3), nitrogen oxides (NO_x), volatile organic compounds (VOC) and carbon monoxide (CO). In this chapter, only the monitoring of ozone is reported on. For information on the monitoring of the other pollutants, the reader is referred to the aforementioned report, and the Report of the Ambient Air Monitoring Working Group (Multistakeholder NO_x/VOC Science Program, 1997).

3.1 MEASUREMENT METHODS

Measurement of ozone by modern continuous analyzers, many of them portable, became prevalent in the 1970s after the methods outlined below were perfected and routine calibration procedures were developed. The importance of ozone monitoring at frequent intervals had been indicated by apparent effects on vegetation and human health in the 1950s, thereby stimulating the installation of urban monitoring networks. These networks, upon which virtually all of the scientific results in this document are based, are gas analyzers which have short cycle times and store ozone readings each minute, often averaging readings within a 1-hour time step. The specifications for these instruments are presented in Table 3.2. Routine network monitoring of ozone is primarily carried out using continuous gas analyzers that operate on the UV light absorption principle.

Chemiluminescence Method

Chemiluminescence-based analyzers are used at some sites. Light is produced from the energy released in a chemical reaction involving ozone and ethylene. The light emission intensity is proportional to the ozone concentration of the air sampled. The energy generated by the reaction is measured by sensitive photodetectors. Chemiluminescence analyzers are referenced to UV photometric-based transfer standards.

Chemiluminescence reaction:

$$O_3 + C_2H_4 \rightarrow O_2 + C_2H_3OH + hv \text{ (430nm)}$$

An issue with the use of these instruments is the leakage or incomplete burning of the ethylene. Since VOC measurements are necessary at most O_3 monitoring sites the presence of ethylene gas or the products of its incomplete combustion may contaminate these other monitoring systems. Although no other common atmospheric pollutants are known to interfere with these analyzers, water vapour can cause a positive interference and must be corrected for during instrument calibration.

Ultraviolet (UV) Photometry Method

These analyzers are based on the fact that O_3 has a strong absorption band (254nm) which coincides with the emission spectrum from low pressure mercury lamps at 253.7nm. This radiation passes through a chamber (tube) containing ambient air. The light is absorbed by ozone is present in the chamber. The amount of UV light depletion is determined by comparing it with that transmitted through a reference chamber with ozone-free air. The ozone concentration is determined using the Beer-Lambert law. The use of the mercury lamp light source is preferred to burning ethylene for the reasons stated above. The analyzers compare O_3 rich and O_3 stripped air (using MnO_2) and calculate the amount of O_3 present in the original sample air flow. Potential atmospheric interferents include hydrocarbons, mercury vapour, SO_2 and styrene.

UV photolytic reaction:

$$O_3 + hv(253.7nm) \rightarrow O_2 + O$$

3.2 INSTRUMENT PERFORMANCE SPECIFICATIONS

Table 3.1 summarizes the commonly used reference methodologies, measurement principles, and performance specifications for network monitoring. These performance specifications are the NAPS QA/QC (Quality Assurance/Quality Control) guidelines.

Table 3.1 Instrument Performance Specifications for Automated Ambient Air Monitoring Methods for Ozone, NOx, VOC and CO.

Pollutant	**Ozone**	**Met Parameters**
Reference Method	Ultraviolet photometry	na[*]
Equivalent Method	Chemi-luminescence	AES protocols[**]
Operating Range	0-1.0 ppm	AES protocols
Minimum Detection Limit	0.005 ppm	na
Noise	0.002 ppm	na
Span Drift -24 hr		
80% of upper range limit	" 5.0%	na
Precision 80% of upper range limit	0.01 ppm	na
Maximum Cycling Time	5 min	1 hour
Averaging Time	1 hour	1 hour

[*] na - Not Available. Information regarding reference methods and traceability to primary standards can be obtained by contacting Environment Canada's NAPS coordinator.

[**] Specifications for meteorological measurements are provided in Mar, 1995.

3.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

3.3.1 *Audit Activities and Protocol*

The NAPS network has a calibration and audit program to ensure that data reported from the network are high quality (Mar, 1995). Multi-point calibrations are done by the local operating personnel, whereas audits are conducted by personnel who are independent of the day-to-day operation of the station being audited. Audits are conducted at the following levels:

- *Instrument audits* are conducted at random once a year by the operating agency to verify the operational characteristics of the instrumentation.
- *Site audits* are conducted at random once a year by the operating agency to verify the accuracy and validity of the siting criteria.
- *Operational audits* are conducted once a year by the operating agency to verify the appropriate procedures involved with the operation of the site.
- *System audits* are conducted to verify the general operation of the national network, including data validation procedures and should be done by an independent body at least every five years or when the particular agency's operational structure undergoes significant changes.

Presently, the NAPS network has an audit program in place to conduct instrument and site audits on the operating agencies once every two years. Most provincial and municipal agencies within Canada also have some form of audit program. The purpose of the NAPS program is to audit the overall performance of the operating agencies rather than that of individual sites.

3.4 EMERGING TECHNOLOGIES

There is considerable work in progress to improve existing or develop new measurement methods and technologies for monitoring ozone and its precursors. The focus of much of this work has been the refinement of such methods to improve detection limits, better address temporal variability, eliminate interference, and decrease costs. Current resources focus on, but are not limited to: optical remote sensing methods; providing continuous or semi-continuous measurements of VOC; improving NO_x and NO_y speciation and detection limits.

The methodologies for ambient monitoring will continue to evolve as more demands are made to increase the understanding of atmospheric chemistry and monitor a wider range of compounds, with lower detection limits or on a continuous basis. Currently, the following aspects (of routine ozone and ozone precursor monitoring) will benefit from emerging technologies:

- routine measurement of low concentrations of NO_x and CO;
- measurement of speciated VOC and NO_y species by more-sensitive and more-cost-effective means;
- remote-sensing monitoring methods;
- improved telecommunication and data manipulation; and
- interference-free methods for aldehyde measurements.

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4 SOURCES

Ozone is not emitted directly, but is formed as a secondary pollutant through atmospheric chemical reactions with the precursors, NO_x (nitrogen oxides) and VOC (volatile organic compounds). Therefore, the sources and fate of ozone's precursors are an important aspect of understanding ozone concentrations. The data for this section come primarily from the Canadian Emissions Inventory of Criteria Air Contaminants, Environment Canada (1996), and from the Draft Report of the Emissions Inventory Working Group (Multistakeholder NO_x/VOC Science Program, 1997).

The 1990 Canadian Emissions Inventory of Criteria Air Contaminants is currently the most recent data available on emissions of ozone precursors (NO_x and VOC). The 1995 Inventory is in preparation but has not yet been released. The inventory provides national summary data as well as provincial emissions data. The inventory provides emissions estimates for approximately 80 different sector sources, which are condensed into 57 sector sources within five major categories (industrial, transportation, miscellaneous, non-industrial fuel combustion and incineration) in the final inventory report.

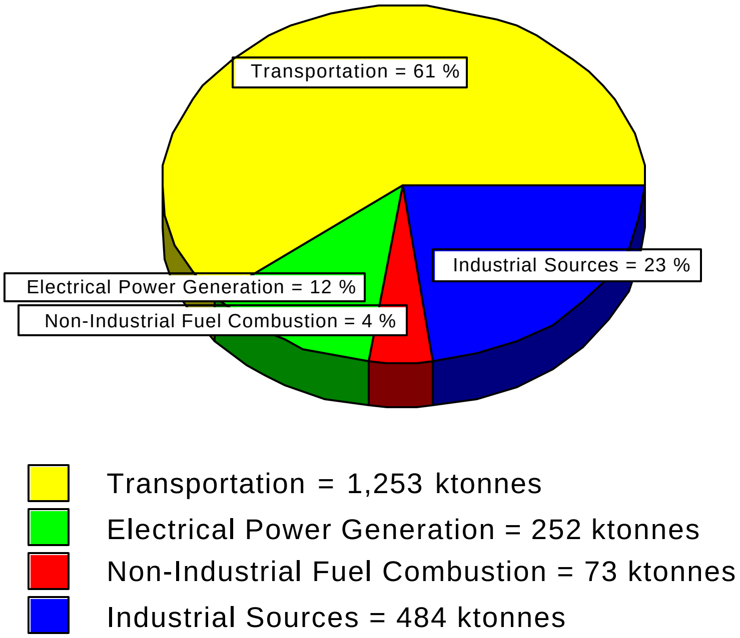
The national emissions inventories are complied by the Pollution Data Branch (PDB) of Environment Canada in collaboration with the provinces and territories. In general, emissions estimates from major industrial sources are compiled by the provinces. The PDB is responsible for compiling data on emissions from the remaining sources, which include anthropogenic and minor industrial sources, the transportation sources, and the fugitive and natural sources.

4.1 NITROGEN OXIDES

Anthropogenic NO_x is the product of stationary and mobile combustion processes. Nitrogen in the fuel source combines with atmospheric oxygen at high temperatures to form several NO_x species of which NO_2 and NO are the most common.

The primary anthropogenic sources of NO_x (Table 4.1) include transportation sources, thermal electrical power plants, and certain industrial processes. Within North America, emissions from the transportation sector and from the electrical utilities plus selected industries account for 98% of total emissions. Within Canada, based upon 1990 emission inventories (Table 4.1), annual NO_x emissions totaled approximately 2.060 million tonnes (2060 ktonnes) with 61% originating from the transportation sector and 23% from the industrial sector. The electric power generating sector produced 12% of national NO_x emissions. (Figure 4.1)

Figure 4.1: 1990 Canadian NO_x emissions by sector (total = 2,060 kilotonnes)



Emissions of NO_x from natural sources account for a small percentage of total emissions. These come from forest fires, lightning and soil microbial activity. The flux of NO_x from the atmosphere to the upper troposphere is very small. Natural NO_x emissions in Canada were estimated at 66kT in 1990, which constituted 3% of the total for anthropogenic and natural sources.

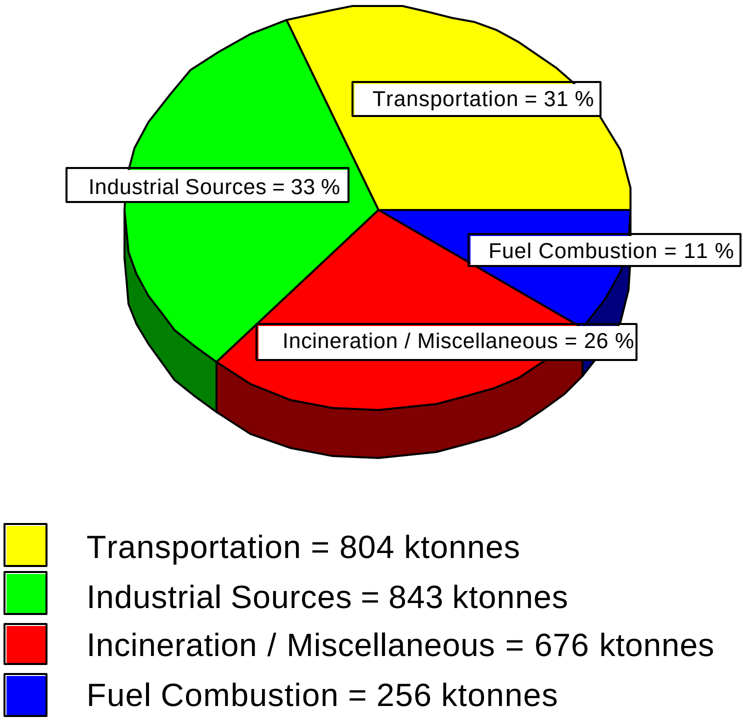
The spatial distribution of NO_x emissions in Canada is shown in Figure 4.3.

4.2 VOLATILE ORGANIC COMPOUNDS

Many hundreds of VOC are included in this category, making generalizations somewhat difficult. VOC are released to the atmosphere by both combustion and evaporation processes. The largest anthropogenic sources of VOC are industrial processes and transportation; other contributors are waste disposal and stationary power plants, compressor stations, etc. Solvent use, petroleum refining and distribution, and chemical manufacturing are the principal industrial sources.

The VOC emission category excludes photochemical non-reactive compounds such as methane, ethane and chloroflurocarbons. In 1990, total Canadian VOC emissions (Table 4.1) were estimated at 2,579 kT (Figure 4.2). The transportation sector produced 31% and the industrial sector 33% of the total emissions. Application of surface coatings, general solvent use and other miscellaneous uses accounted for 24% of VOC emissions. Light duty gasoline car and truck emissions were 22% of the total with 21% produced by upstream oil and gas operations. The distribution of these emissions is shown in Figure 4.4.

Figure 4.2: 1990 Canadian VOC emissions by sector (total = 2,579 kilotonnes)



Biogenic emissions of VOC are mainly from vegetation, usually in the warmer growing season. Isopenes from deciduous forests and monoterpenes from coniferous forests are the important compounds involved in ozone formation.

Biogenic VOC were estimated at 14,644kT in 1990 (Environment Canada 1996) with vegetation contributing 97% of the total. This is about 5.5 times the total anthropogenic contribution of VOC. Within the three ozone problem areas, however, anthropogenic VOC emissions exceed biogenic emissions but biogenic emissions are 2.8 times more reactive than anthropogenic ones. The distribution of biogenic VOC emissions in Canada is shown in Figure 4.5.

Table 4.1 1990 Anthropogenic Emissions of Common Pollutants for Canada

	Emissions in Tonnes	
Category / sector	**NOx**	**VOC**
Industrial Sources		
ABRASIFS MANUFACTURE	214	1,758
ALUMINUM PRODUCTION	3,173	834
ASBESTOS PRODUCTION	895	45
ASPHALT PRODUCTION	260	2,206
BAKERIES	4	3,459
CEMENT AND CONCRETE MANUFACTURE	29,372	186
CLAY PRODUCTS	292	26
COAL INDUSTRY	1,824	2,457
CRUDE OIL PRODUCTION	2,952	4,390
FERROUS FOUNDRIES	30	1,106
GRAIN INDUSTRIES	10	1
IRON AND STEEL PRODUCTION	29,069	27,294
IRON ORE MINING AND BENEFICIATION	6,809	562
MINING AND ROCK QUARRYING	3,243	142
NATURAL GAS PROCESSING	117,489	3,664
NON-FERROUS MINING AND SMELTING	54,594	329
OIL SANDS	15,855	30
OTHER CHEMICALS	15,102	2,818
OTHER PETROLEUM AND COAL PRODUCTS	458	116
PAINT & VARNISH MANUFACTURING	9	1,236
PETROCHEMICAL INDUSTRY	12,990	28,662
PETROLEUM REFINING	33,466	82,264
PLASTICS & SYNTHETIC RESINS FABRICATION	354	12,477
PULP AND PAPER INDUSTRY	61,388	20,165
UPSTREAM OIL & GAS OPERATIONS	3,159	541,874
WOOD INDUSTRY	5,419	15,958
OTHER INDUSTRIES	85,322	88,575
Category total:	**483,751**	**842,636**
Non Industrial Fuel Combustion		
COMMERCIAL FUEL COMBUSTION	24,192	1,055
ELECTRIC POWER GENERATION	252,356	2,280
RESIDENTIAL FUEL COMBUSTION	34,971	2,616
RESIDENTIAL FUEL WOOD COMBUSTION	5,462	250,526
Category total:	**316,982**	**256,478**

Table 4.1 cont. 1990 Anthropogenic Emissions of Common Pollutants for Canada

	Emissions in Tonnes	
Category / sector	**NOx**	**VOC**
Transportation		
AIRCRAFT	18,506	7,252
HEAVY-DUTY DIESEL VEHICLES	324,277	36,555
HEAVY-DUTY GASOLINE TRUCKS	11,943	11,445
LIGHT DUTY GASOLINE TRUCKS	95,323	137,294
LIGHT DUTY GASOLINE VEHICLES	294,501	441,800
LIGHT-DUTY DIESEL TRUCKS	2,610	1,088
LIGHT-DUTY DIESEL VEHICLES	1,959	679
MARINE	47,346	32,174
MOTOR CYCLES	540	3,023
OFF-ROAD USE OF DIESEL	271,643	27,763
OFF-ROAD USE OF GASOLINE	47,153	95,747
PROPANE POWERED VEHICLES	2,803	1,674
RAILROADS	134,143	6,599
TIRE WEAR	0	815
Category total:	**1,252,748**	**803,908**
Incineration		
OTHER INCINERATION	2659	2594
WOOD WASTE INCINERATION	4882	52898
Category total:	**7,541**	**55,492**
Miscellaneous		
APPLICATION OF SURFACE COATINGS	4	177,520
CIGARETTE SMOKING	0	0
DRY CLEANING	1	11,985
FUEL MARKETING	0	96,654
GENERAL SOLVENT USE	9	289,888
MARINE CARGO HANDLING INDUSTRY	0	1
PESTICIDES AND FERTILIZER APPLICATION	746	42,113
STRUCTURAL FIRES	514	2,376
Category total:	**1,275**	**620,538**
TOTAL FOR CANADA	**2,062,297**	**2,579,051**

* The Carbon Black Sector was grouped under the Other Industries Sector to protect the confidentiality of the information.

Figure 4.3 Distribution of 1990 annual NOx emissions in Canada

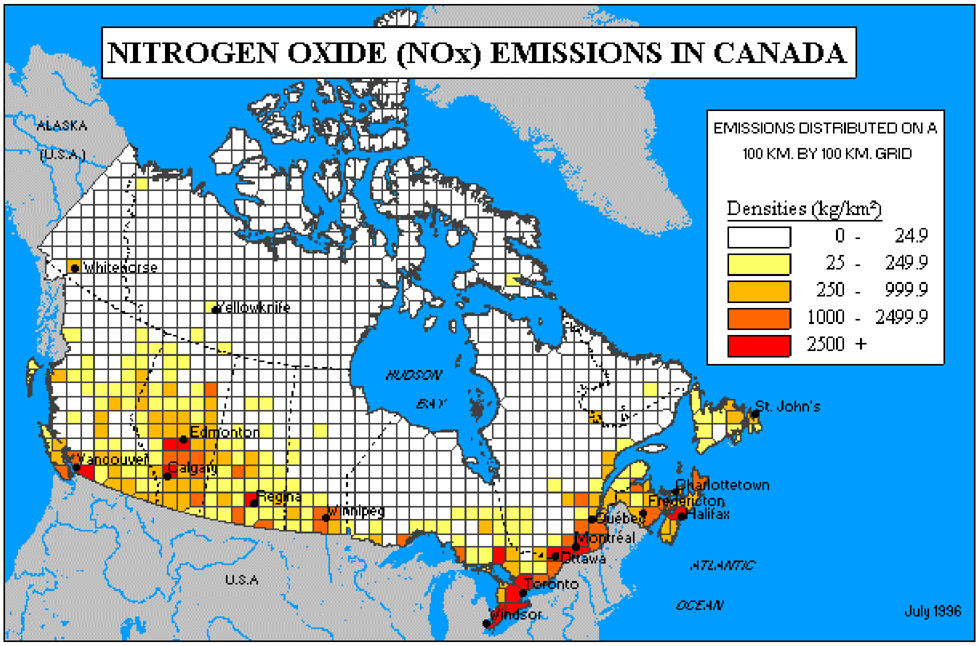


Figure 4.4 Distribution of 1990 anthropogenic VOC emissions in Canada

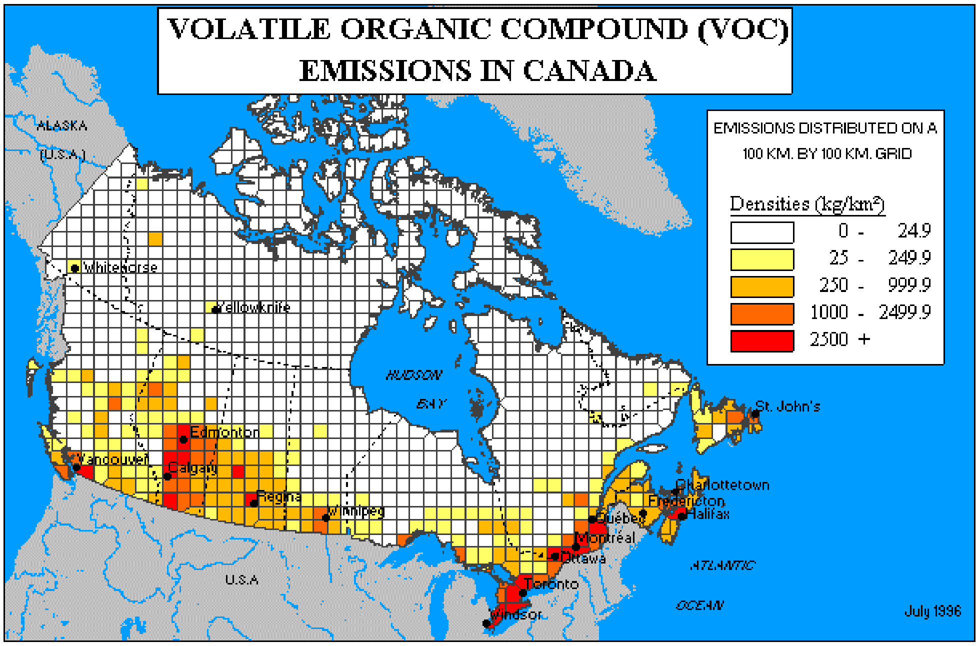
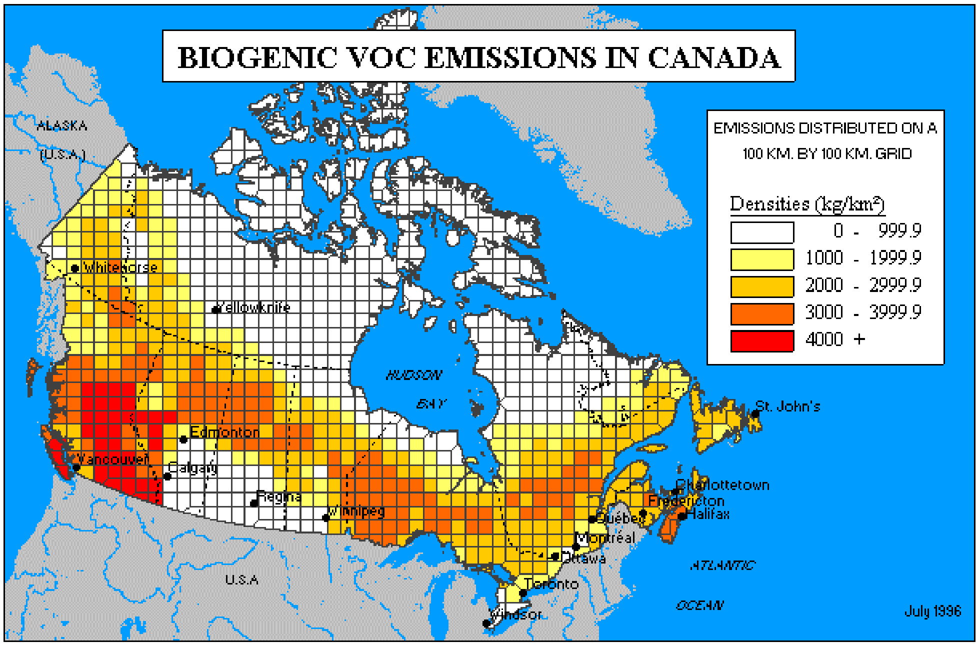


Figure 4.5 Distribution of 1990 biogenic VOC emissions in Canada



4.3 UNCERTAINTIES IN EMISSIONS INVENTORIES

Emission inventory reporting in Canada is voluntary in most provinces with statistics for larger single sources being more accurate than smaller, more widely distributed sources. Estimates of overall accuracy suggest a "20% range of uncertainty for NO_x. VOC information is less accurate that that for NO_x, however, the overall proportion of sources provides a general pattern that should be confirmed for any area which requires closer study. The 1995 Environment Canada inventory is expected to be more accurate than the figures presented here.

REFERENCES

Environment Canada (1996). Canadian Emissions Inventory of Criteria Air Contaminants (1990). Report EPS 5/AP/7E; 75p.

Multistakeholder NO_x/VOC Science Program, (1997). Draft Report of the Emissions Inventory Working Group.